

Europäisches Patentamt **European Patent Office**

Office européen des brevets

Bescheinigung

Certificate

Attestation

REC'D 1 0 JAN 2005

WIPO

IPO BOT

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein. The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr.

Patent application No. Demande de brevet n°

04075984.7

PRIORITY

DOCUMENT

SUBMITTED OR TRANSMITTED IN

COMPLIANCE WITH RULE 17.1(a).OR (b)

Der Präsident des Europäischen Patentamts; Im Auftrag

For the President of the European Patent Offic

Le Président de l'Office européen des brevets p.o.

R C van Dijk

BEST AVAILABLE COPY



Anmeldung Nr:

Application no.:

04075984.7

Demande no:

Anmeldetag:

Date of filing: 31.03.04

Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

DSM IP Assets B.V. Het Overloon 1 6411 TE Heerlen PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention: (Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung. If no title is shown please refer to the description. Si aucun titre n'est indiqué se referer à la description.)

A method, an immersion fluid and an apparatus for producing micro-chips

In Anspruch genommene Prioriät(en) / Priority(ies) claimed /Priorité(s) revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/Classification internationale des brevets:

G03F7/00

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL PL PT RO SE SI SK TR LI

21813EP/P2/

-1-

A METHOD, AN IMMERSION FLUID AND AN APPARATUS FOR PRODUCING MICROCHIPS

5

25

30

35

The invention relates to a method, an immersion fluid and an apparatus for producing microchips by using immersion lithography.

Since the invention of integrated circuits in 1959, the computing power of microprocessors has been doubled every 18 months and every three 10 years a new generation of microchips has been introduced, every time reducing the size of electronic devices. This phenomenon is known as Moore's law. The performance of the microchip is, to a large degree, governed by the size of the individual circuit elements in the microchip. A microchip in general comprises as the circuit elements a complex three-dimensional structure of alternating. 15 patterned layers of conductors, dielectrics, and semiconductor films. As a general rule, the smaller the circuit elements, the faster the microchip and the more operations it can perform per unit of time. This phenomenal rate of increase in the integration density of the microchips has been sustained in large by advances in optical lithography, which has been the method of choice for producing the 20 microchips.

A higher degree of integration of the circuit requires a shorter wavelength of exposure light used in the method of producing microchips by optical lithography. Changing of the exposure light to shorter wavelengths has indeed been the method of choice to increase the resolution. However, switching to shorter wavelengths is becoming increasingly a daunting task as new exposure tools and materials such as photo-resists must be designed. This is a difficult task and it often results in implementation issues and delays. Therefore chip manufacturers generally tend to postpone the introduction of a new exposure wavelength as long as possible and attempt to prolong the lifetime of an existing technology using alternative approaches. Already for a period of time immersion lithography is considered to be an effective method to improve the resolution limit of a given exposure wavelength. Here the air between the bottom lens and silicon wafer in an apparatus is replaced with a fluid, leading essentially to a decrease in effective wave length, see for example: A. Takanashi et al. US Patent No.

15

20

25

30

35

4480910 (1984). The fluid should i.a. have a high transparency, it must not influence the chemistry of the photoresists used to produce the microchip, it must not degrade the surface of the lens.

Immersion lithography is for example possible for the
wavelengths 248 nm, 193 nm and 157 nm. Because of its transparency at 248 nm and 193 nm water is the main candidate for immersion fluid at this wavelength.
(See for example: J.H. Burnett, S. Kaplan, Proceedings of SPIE, Vol. 5040, P. 1742 (2003). Because of exceptional transparency of fluorinated and siloxane-based compounds at 157 nm, such fluids are being considered for 157 nm immersion lithography.

Aim of the invention is to provide a method for producing microchips by using immersion lithography showing further resolution enhancement.

Surprisingly this aim is achieved because the immersion fluid comprises an additive so that the refractive index of the immersion fluid is higher than the refractive index of the fluid not comprising the additive.

Preferably the refractive index of the immersion fluid is at least 1% higher, more preferably at least 2% higher, still more preferably at least 5% higher, most preferably at least 10% higher.

Two types of additives may be added. Additives, which are soluble in the base liquid, and additives, which are insoluble and therefore must be dispersed as particles, preferably nano particles, in the base liquid. As soluble additives, both organic compounds and liquids, and inorganic (salts) may be used. In case of water as fluid, examples of organic compounds include: various types of sugars, alcohols such as for example cinnamyl alcohol and elthylene glycol, 2-plcoline, ethoxy-(ethoxy-ethyl-phosphinothioylsulfanyl)-acetic acid ethyl ester, 1-fluoro-1-(2-hydroxy-phenoxy)-3-methyl-2,5-dihydro-1H-1\(\lambda\)5-phosphol-1-ol and water soluble functionalised silicon oil. Examples of inorganic salts include: mercury monosulphide, mercury(I) bromide, marcasite, calcite, sodium chlorate, lead monoxide, pyrite, lead(II) sulfide, copper(II) oxide, lithium fluoride, tin(IV) sulphide, lithium niobate and lead(II) nitrate. As insoluble compounds in water as well as in fluorinated and siloxane basedfluids both inorganic, organic, and metallic nano particles may be used. The weight average size of the particles is preferably 10 times, more preferable 20 times, and even more preferably 30 times, and even more preferably 40 times smaller than the corresponding

5

10

15

20

25

30

35

exposure wavelength. In case of water as the immersion fluid the size of the nano particles may be less than 100 nanometer (nm), preferably less than 50 nm, more preferably less than 30 nm, still more preferably less than 20 nm, most preferably less than 10 nm. This results in a high transparency of the immersion fluid.

The volume percentage of the nano particles in the fluid is preferable at least 10%, more preferably at least 20%, still even more preferably at least 30%, even still more preferably at least 40%. Most preferably the volume percentage is at least 50%, as this results in a fluid having a high refractive index. a high transparency and low amount of scattering of the Incident light. Examples of inorganic and metallic nano particles include: Alumina, Aluminum, Aluminium nitride, Aluminium oxide, Antimony pent oxide, Antimony tin oxide, Brass, Calcium carbonate, Calcium chloride, Calcium oxide, Carbon black, Cerium, Cerium oxide, Cobalt, Cobalt oxide, Copper, Copper oxide, Gold, Hastelloy, Hematite- (alpha, beta, amorphous, epsilon, and gamma), Indium, Indium tin oxide, Iron, Iron-cobalt alloy. Iron-nickel alloy, Iron oxide, Iron oxide, transparent, Iron sulphide, Lanthanum, Lead sulphide, Lithium manganese oxide, Lithium titanate, Lithium vanadium oxide, Luminescent, Magnesia, Magnesium, Magnesium oxide, Magnetite, Manganese oxide, Molybdenum, Molybdenum oxide, Montmorillonite clay, Nano oxide suspensions, Nickel, Niobia, Niobium, Niobium oxide, Silicon carbide, Silicon dioxide, Silicon nitride, Silicon nitride, Yttrium oxide, Silicon nitride, Yttrium oxide, Aluminium oxide, Silver, Specialty, Stainless steel, Talc, Tantalum, Tin, Tin oxide, Titania, Titanium, Titanium diboride, Titanium dioxide, Tungsten, Tungsten carbide- cobalt, Tungsten oxide, Vanadium oxide, Yttria, Yttrium, Yttrium oxide, Zinc, Zinc oxide, Zirconium, Zirconium oxide and Zirconium silicate.

In a preferred embodiment nano particles comprising Al^{3+} -compounds are used in the immersion fluid of the process according to the invention. This is because such an immersion fluid has not only a very high refractive index, but is also highly transparent. Good examples of such particles include Al_2O_3 and $Al(OH)_3$.

In this case good results are obtained of the immersion fluid comprises 25 - 45 vol.% of the nano particles comprising the Al³⁺-compound are used. More preferably 30 - 40 vol.% of the particles is used.

Such an immersion fluid not only has favorable optical properties, like a high refractive index and a high transparency, but is also good

31. MAA. 2004 14.07

-4-

processable in the standard apparatus for producing microchips. For example the viscosity is low enough, so that the immersion fluid can be pumped easily.

It is known to the skilled person how to make stabile dispersions of the nano particles in fluids like water.

In a further preferred embodiment a fluid is used comprising transparent particles having a refractive index higher than the refractive index of the pure fluid and the additive in an amount, such that the refractive index of the fluid comprising the additive is equal to the refractive index of the transparent particles.

5

10

15

20

35

The fluid comprising the transparent particles has a very high transparency.

The transparency of the material of the transparent particles may be at least 40%. Preferably this transparency is at least 60%, more preferably at least 80%, still more preferably at least 90 %, most preferably at least 95%. Examples of suitable transparent particles are particles of transparent crystals, for example SiO₂, Al₂O₃ and HfO₂. Preferably quarts or saphire particles are used.

The transparent particles may have a diameter of at least 25 nm, Preferably the diameter of the particles is at least 50 nm. The transparent particles may have a diameter of less than 1000 nm, Preferably the diameter of the particles is less than 500 nm, more preferably less than 300 nm, still more preferably less than 250 nm, most preferably less than 200nm. If particles in this range of sizes are used, they are easy to produce.

25 be used. Preferably an additive that is soluble in the fluid is used (such as cesium sulphate). As the particles are highly transparent reduction of transparency because of use of the additive is reduced. This is especially true if the fluid comprises a high volume fraction of the particles such as quartz. The upper limit of the volume fraction of transparent particles depends on the possibility to handle the fluid. As the refractive index of both the transparent particles and the fluid comprising the additive is equal, there is hardly any or no disruption of optical properties.

In a further preferred embodiment a fluid is used comprising transparent particles having a refractive index higher than the refractive index of the pure fluid and a very narrow particle size distribution. Such particles can be

-5-

grown from seed nanoparticles by controlled deposition of material on these seeds (as known to the skilled person). Preferably the coefficient of variation as determined by high resolution TEM is less than 10%, more preferably less than 5%, even more preferably less than 2% most preferably less than 1%.

The invention also relates to the immersion fluid.

The invention also relates to an apparatus for immersion lithography for the production of microchips, comprising the immersion fluid.

CLAIMS

- Method for producing microchips by using immersion lithography,
 characterised in that the immersion fluid comprises an additive so that
 the refractive index of the immersion fluid is higher than the reflective index of the fluid not comprising the additive.
 - Method for producing microchips according to claim 1, characterised in that the refractive index is at least 1% higher.
- Method according to claim 1 or 2, characterised in that the fluidcomprises nano particles.
 - 4. Method according to claim 3, characterized in that the particles have a diameter that is 10 times smaller than the wavelength of the exposure light.
- Method according to any of claims 1-4, characterised in that the fluid
 comprises at least 10 volume % of nano particles.
 - 6_ Method according to any of claims 1-4, characterised in that the fluid comprises at least 50 volume % of nano particles.
- 7. Method according to any one of claims 1-6, characterized in that the fluid comprises transparent particles having a refractive index higher than the refractive index of the pure fluid and the additive in an amount, such that the refractive index of the fluid comprising the additive is equal to the refractive index of the transparent particles.
- 8. Method according to any one of claims 1-7, characterized in that the fluid comprises transparent particles having a refractive index higher than the refractive index of the pure fluid and the additive in an amount, such that the refractive index of the fluid comprising the additive is equal to the refractive index of the transparent particles and the particles have a monodisperse particle size distribution with coefficient of variation less than 10%.
- 30 9. Immersion fluid as used in the method according to any one of claims 1-8.
 - 10. Apparatus for producing microchips, based on the technology of immersion lithography, characterised in that the apparatus comprises the immersion fluid as used in the process of any one of claims 1-6.

-7-

ABSTRACT

Method for producing microchips by using immersion lithography, wherein the immersion fluid comprises an additive so that the refractive index of the immersion fluid is increased relative to the fluid not comprising the additive. The exposure light in the method has improved resolution, so that microchips having an increased integration density are obtained. The invention also relates to the immersion fluid and an apparatus for immersion lithography, comprising the immersion fluid.

PCT/**EP**20**04**/0**12248**

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

D BLACK BORDERS
IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
FADED TEXT OR DRAWING
☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
☐ SKEWED/SLANTED IMAGES
☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
☐ CRAY SCALE DOCUMENTS
LINES OR MARKS ON ORIGINAL DOCUMENT
\square REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
□ OTHER:

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.